

SURVEY OF MODERN ELECTROANALYTICAL METHODS

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The recent thrust of electroanalytical techniques has been primarily directed toward analysis of the nature of electrode processes rather than toward evaluation of solution concentrations. As an aid in accomplishing this goal, a whole series of new methods have been developed. The first group, involving semi-infinite diffusion, can be classified into two broad categories by the size of the excitation signal ("large" and "small" amplitude), and then each can be further sub-classified according to the form (shape, periodicity, etc.) of the excitation signal and occasionally according to the monitored response. Ideally, the small amplitude cases are those where the excitation signal is sufficiently small that the perturbation introduced can be considered linear. Nevertheless, those cases where the excitation signal is small, but primary attention is given to minute non-linear effects, are considered in this group. The aforementioned excitation signal is an impressed voltage, current, or, in some cases, a combination of these which is experimentally applied over a time interval. This signal, in turn, evokes from the system a response signal of the complementary electrical variable whose amplitude and time dependency reflects the composition and nature of the electrochemical system under consideration. This response signal, in whole or in part, is then converted into a monitored response by electrical, mechanical, or graphical means and is displayed unchanged, or in differential or integral form, as a function of t , $t^{1/2}$, E , or some other convenient parameter. The presentation is suggested by theory and ameliorated by instrumentation. In this manner, the effect of chemical kinetic complications, such as pre-kinetic, post-kinetic, catalytic, or successive reactions can be exaggerated and the evaluation simplified. Similar principles facilitate the evaluation of adsorption phenomena and electron-transfer rates. The following figures (prepared by William Heineman and Thomas Ridgway of this laboratory) indicate some, but by no means all, of the methods currently available and utilized.

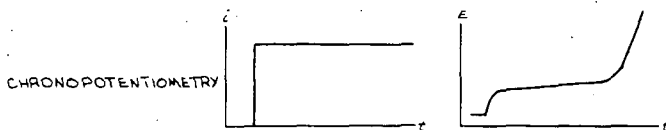
Thin-film and thin-layer electrodes offer several interesting avenues in electrochemical investigations. Both involve diffusion across a thin film or layer; with a thickness of 10^{-3} to 10^{-2} cm., essentially homogeneous mixing is accomplished by simple diffusion in 0.1 to 10 seconds. For the latter technique, a thin layer of sample solution is confined between two boundaries, at least one of which is a working electrode. This system has been applied to rapid controlled-potential coulometry and to the study of adsorption and post-kinetic reactions. When both boundaries are independent working electrodes, several approaches to the study of chemical events occurring in the thin layer are possible. Chemical changes initiated at one electrode may be observed or modified at the other electrode with only a small time lag. Also rapid attainment of steady-state current is achieved where an oxidation occurs at one electrode and the corresponding reduction at the other.

Some interesting applications of the technique are:

1. establishment of diffusion coefficients;
2. steady-state current as a function of the potentials of the two electrodes: steady-state "voltammetry";
3. rapid controlled-current or controlled-potential coulometric titrations in the thin layer;
4. study of the products of electrode reactions; intermediate oxidation states, metastable products, adsorption isotherms of products, etc.;
5. kinetics of chemical reactions in the solution layer;
6. photolysis and spectrophotometry in the thin layer.

I. LARGE AMPLITUDE ELECTROANALYTICAL TECHNIQUES

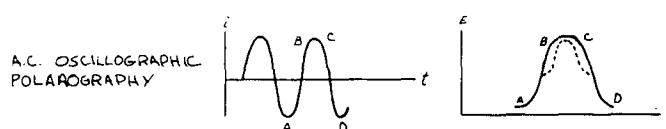
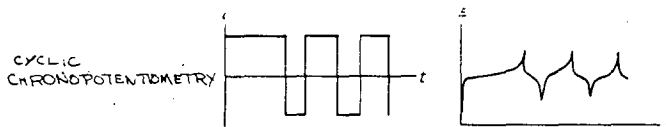
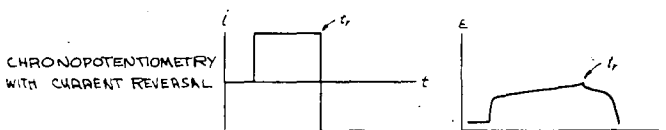
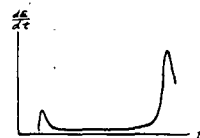
NAME	EXCITATION SIGNAL	SYSTEM RESPONSE SIGNAL	MONITORED RESPONSE
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CONTROLLED CURRENT

DERIVATIVE CHRONOPOTENTIOMETRY

SAME

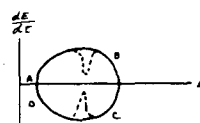
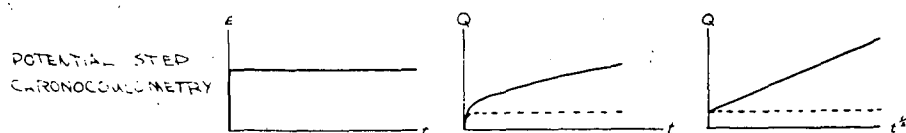
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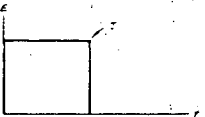
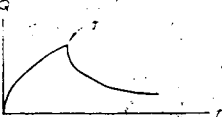
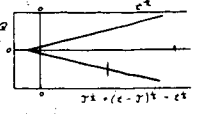
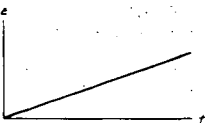
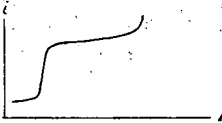
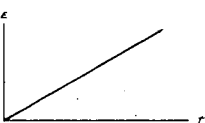
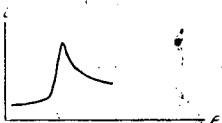
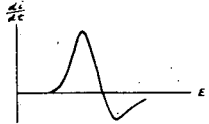
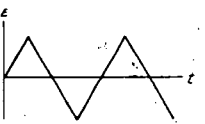
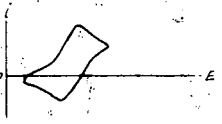
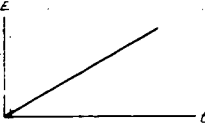
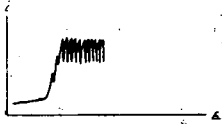

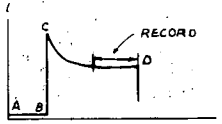

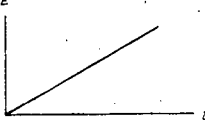
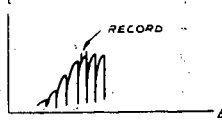
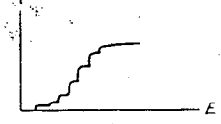
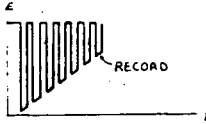
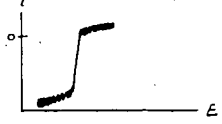


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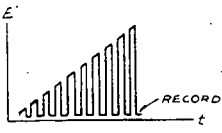

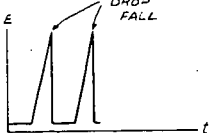
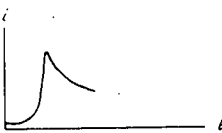
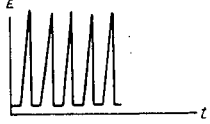
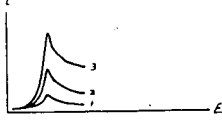
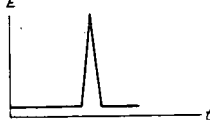
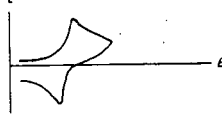
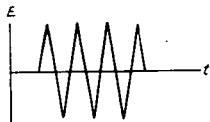
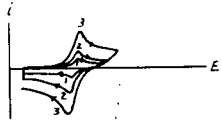
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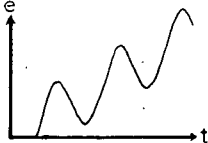
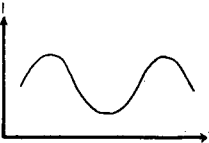
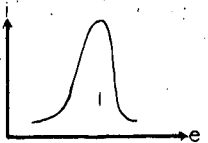
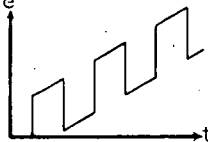
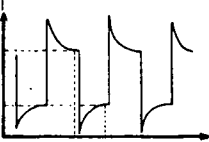
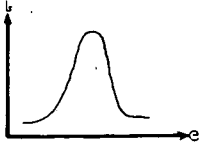
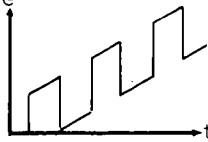

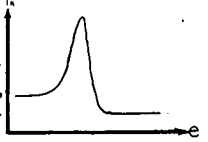

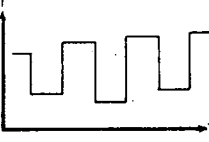
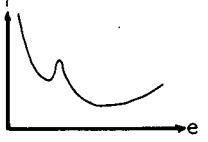
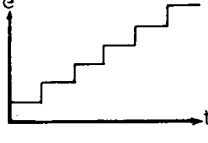
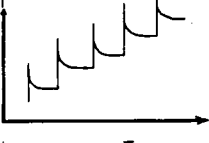
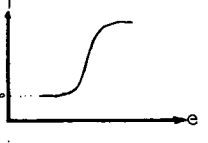
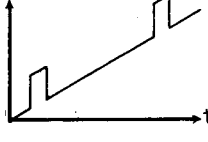


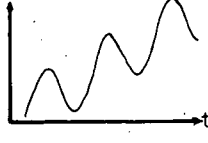
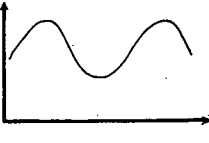
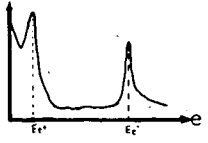
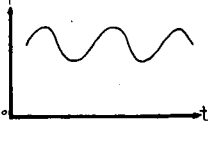
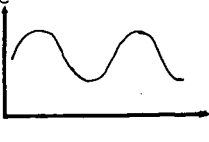

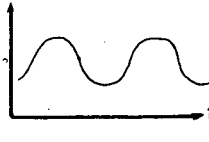
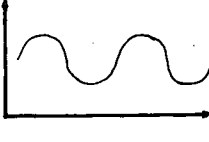
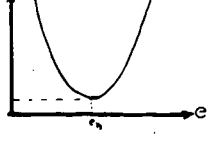
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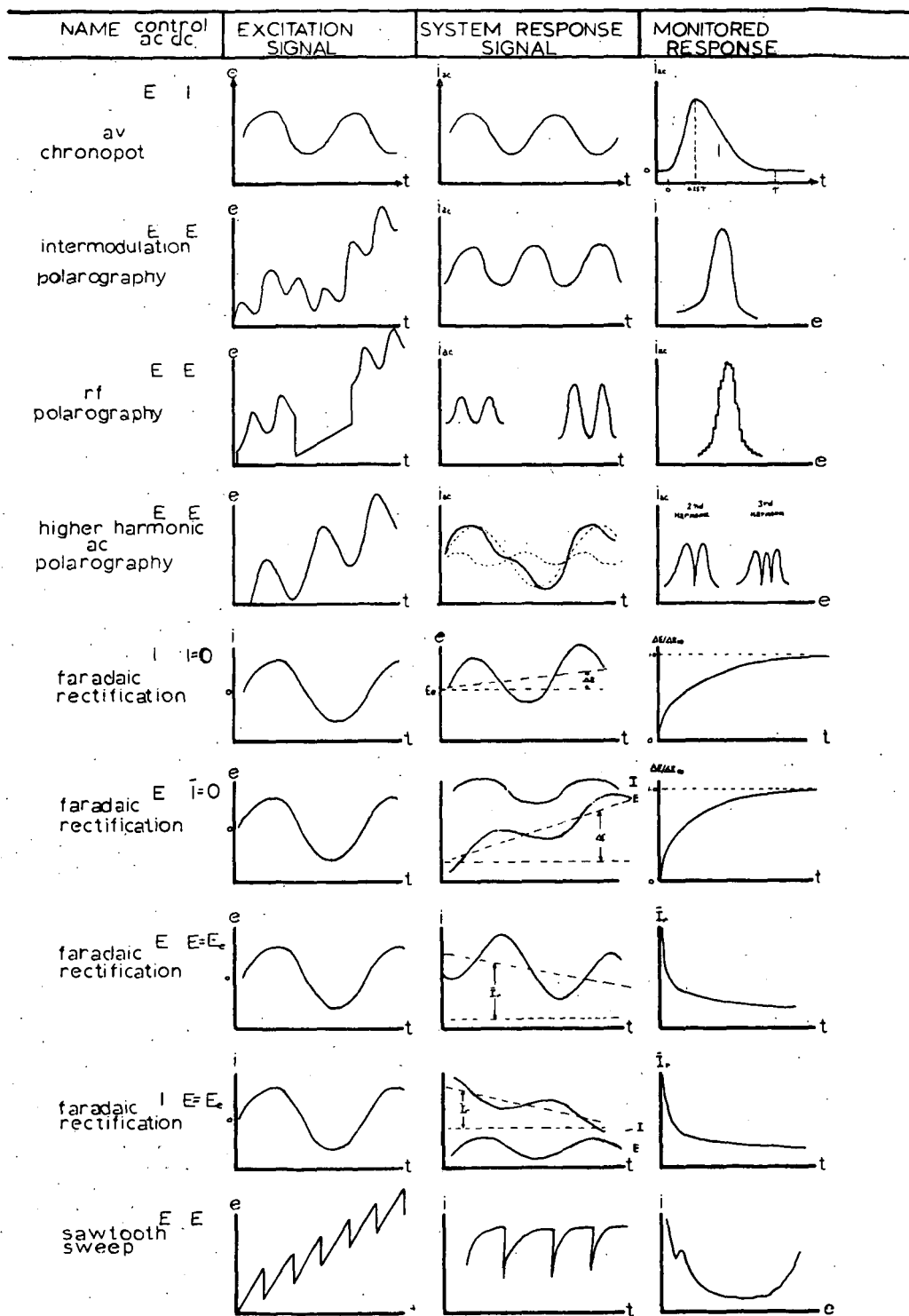
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VOLTAMMETRY			
CHRONOAMPEROMETRY WITH POTENTIAL SWEEP			
DERIVATIVE VOLTAMMETRY	SAME	SAME	
CYCLIC VOLTAMMETRY			
POLAROGRAPHY			
PULSE POLAROGRAPHY			
FAST POLAROGRAPHY			
ALOUSEK I			


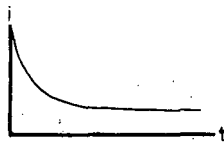

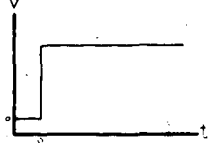
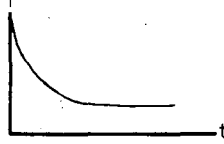
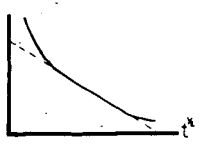
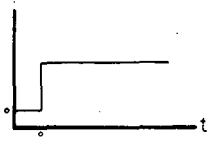

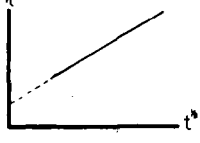
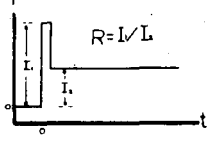
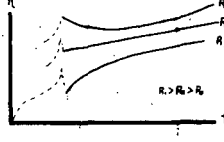
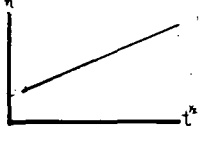
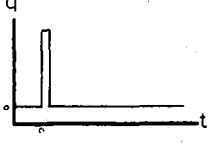
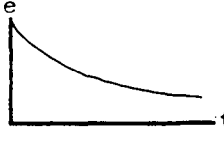
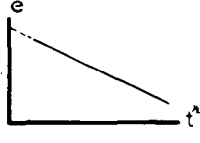
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SINGLE - SWEEP OSCILLOGRAPHIC POLAROGRAPHY			
MULTISWEEP OSCILLOGRAPHIC POLAROGRAPHY			
TRIANGULAR - WAVE OSCILLOGRAPHIC POLAROGRAPHY			
CYCLIC TRIANGULAR - WAVE OSCILLOGRAPHIC POLAROGRAPHY			

II. SMALL AMPLITUDE ELECTROANALYTICAL TECHNIQUES

NAME	control ac dc	EXCITATION SIGNAL	SYSTEM RESPONSE SIGNAL	MONITORED RESPONSE
ac polarography	E E			
square wave polarography	E E			
Kalousek III polarography	E E			
triangular wave polarography	E E			
staircase polarography	E E			
derivative pulse polarography	E E			
tensammetry	E E			
ac chronopot	I I			
av polarography	I E			



NAME control dc	EXCITATION SIGNAL	SYSTEM RESPONSE SIGNAL	MONITORED RESPONSE
<p>E</p> <p>potentiostatic</p>			
<p>V</p> <p>voltastatic</p>			
<p>I</p> <p>galvanostatic single pulse</p>			
<p>I</p> <p>galvanostatic double pulse</p>			
<p>Q</p> <p>coulostatic</p>			
<p>E</p> <p>integral potential step</p>	